Deoxygenation of decanoic acid and its main intermediates over unpromoted and promoted sulfided catalysts

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ABSTRACT

The transformation of decanoic acid, used as a model oxygenated compound, was first studied over Mo/Al_2O_3 at 340 °C under 4 MPa of total pressure (H_2 pressure equal to 2.72 MPa) in a fixed-bed reactor. The deoxygenation of decanoic acid is considered to proceed through two main routes: (i) the HDO pathway yielding decenes and decane as ultimate hydrocarbons, oxygen being removed as water; (ii) the DEC pathway involving a decarbonylation reaction and mainly leading to nonene isomers, oxygen being discarded as water and carbon monoxide. Other products such as oygenates (mainly decanal and 1-decanol) and sulfur-containing products (mainly 1-decanethiol) appeared as intermediates of the HDO way. A significant inhibiting effect of carboxylic acid on the deoxygenation of decanal was highlighted. A general reaction scheme of deoxygenation of decanoic acid over sulfided catalysts was established. Considering a sulfur vacancy as an active site, deoxygenation reaction mechanisms were proposed involving a cationic species as a common intermediate between the HDO and the DEC pathways. The effect of Co and Ni on the deoxygenation rate of decanoic acid was measured by using both $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$. The DEC route was strongly promoted by Co and Ni, whereas an inhibiting effect of Co and Ni was observed on the HDO route. It was assumed that the promoter effect on the DEC route may result from an increase of the basicity of sulfur anions neighbouring of Co or Ni present in the sulfided promoted phase.

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1. Introduction

The development of bio-fuels is considered as a very promising industrial way to decrease the consumption of fossil fuels and hence to reduce the global emission of carbon dioxide. For this purpose, since 2009, European Union promotes the use of non-food biomass (cellulosic and lignocellulosic materials) which can be converted into renewable liquid fuels by appropriate processes [1]. Flash pyrolysis is the most widely applied process for the production of bio-oils [2–4]. Nevertheless, the so-obtained liquids as transportation fuels have poor physico-chemical properties (high viscosity, thermal and chemical instability, weak engine efficiency, etc.) due to their high content of oxygen (35–40 wt%) [2]. Therefore, upgrading of these bio-oils is required to reduce the quantity of oxygenated organic compounds (aldehydes, ketones, acids, esters, phenol derivatives, etc.). Hydrotreatment process using sulfided catalysts is reported to decrease the amounts of oxygenated compounds in bio-oils [5–11]. Due to the similarity of this process with existing hydrotreatment processes in petroleum refinery, i.e.

hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), the development of a co-hydrotreatment process of bio- and fossil oils has been considered by several authors [12–20].

Phenolic molecules have been often used as model oxygenated molecules in most of the studies related to hydrodeoxygenation reactions [21–29]. However, the study of carboxylic acid deoxygenation is also of fundamental interest. Indeed, carboxylic acids are important constituents of the oxygenated fraction in liquids produced by Fisher-Tropsch synthesis [11,30]. In addition, the pyrolysis of hemicellulose and cellulose raw materials leads to liquids containing carboxylic acids in large amounts (up to 25 wt%) [31,4]. Moreover, esters are components of vegetable oils which can be used as a green motor fuel after their deoxygenation [32–36], and it is well known that carboxylic acids are intermediate products of the deoxygenation of esters when their deoxygenation is performed over sulfide catalysts [37–41]. For these reasons, the deoxygenation of carboxylic acids, which has been studied over both sulfided [20,37–39,42], reduced Ni/SiO_2 [43] and supported Cu-based catalysts [44], is of current interest.

It can be assumed that the deoxygenation of carboxylic acids proceeds through three different pathways over sulfided catalysts: hydrodeoxygenation (HDO), decarbonylation and decarboxylation [8,12]. Deoxygenated hydrocarbons obtained by the HDO route

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contain the same number of carbon atoms as the starting carboxylic acid, oxygen being eliminated as water. On the other hand, hydrocarbons obtained by decarbonylation and/or decarboxylation contain less carbon than the parent carboxylic acid since one atom of carbon is removed as carbon oxides (CO and/or CO_2).

In the specific case of heptanoic acid, its deoxygenation reaction was studied over supported sulfided catalysts ($NiMo/Al_2O_3$ and $CoMo/Al_2O_3$) at 250 °C under 1.5 MPa of total pressure [38]. In accordance with the deoxygenation routes described above, C7 (heptenes and heptane) and C6 hydrocarbons (hexenes and hexane) were obtained. Whatever the catalyst used, C7 hydrocarbons were the main deoxygenated products in absence of a sulfur-containing compound in the liquid feed, showing that the HDO route was predominant. However, the selectivity towards alkane and alkene depended on the nature of the catalyst. Then, $NiMo/Al_2O_3$ was reported to be more selective towards alkanes (heptane and hexane), while $CoMo/Al_2O_3$ led to a higher selectivity towards alkenes (heptenes and hexenes). In addition, the authors reported that $NiMo/Al_2O_3$ was about twice more active than $CoMo/Al_2O_3$. Using unsupported transition metal sulfide catalysts (MoS_2, Ni_3S_2 and Ni-promoted MoS_2), Ruinart de Brimont et al. [41] confirmed the occurrence of the deoxygenation routes of heptanoic acid. Indeed, under identical experimental conditions (250 °C, 1.5 MPa), the same deoxygenated products, C6 and C7 hydrocarbons, were observed. However, their quantities strongly depended on the use of unpromoted (MoS_2) or promoted (Ni-MoS_2) catalysts. Indeed, the unsupported MoS_2 phase promoted the formation of C7 hydrocarbons (mainly heptane). On the contrary, hexenes were the main deoxygenated products over NiMoS catalysts indicating a significant effect of the presence of nickel on the selectivity of sulfided catalysts. These results show that the DEC pathway (route one, as described above) was significantly improved when the reaction was performed over nickel promoted catalysts. It should be noticed that the authors added dimethyl disulfide as a precursor of H_2S to the liquid feed. Thus, it was reported that H_2S modified the selectivity of such catalysts: it shifted the main products from C7 to C6 hydrocarbons, thus reducing the contribution of the HDO route in the transformation of carboxylic acid [39]. Decanoic acid was also used as a probe carboxylic acid. Deoxygenation reaction of this molecule was studied over $CoMoP/Al_2O_3$ [20] and $NiMo/Al_2O_3$ [37]. In both cases, predominant formation of nonane compared to decane was observed, showing that the MoS_2 phase promoted by Ni or Co atoms favoured the deoxygenation reaction of carboxylic acid through decarbonylation and/or decarboxylation reactions, rather than by the HDO route which led to decane.

In the present work, the transformation of decanoic acid was studied over an unpromoted (Mo/Al_2O_3) and promoted ($NiMo/Al_2O_3$ and $CoMo/Al_2O_3$) catalysts under the conditions close to those of a hydrotreatment process (fixed-bed reactor, 4 MPa, 340 °C). The reactivity of the main reaction intermediates (decanal, 1-decanol, 1-decanethiol) was also studied over the unpromoted catalyst in order to establish the reaction scheme of deoxygenation of decanoic acid over these kinds of materials. The experimental results obtained over the different catalysts (promoted and unpromoted), allowed to propose the reaction mechanisms involved in such a reaction, the role of the promoters (Co and Ni) was also discussed. Owing to demonstrate the strong adsorption of carboxylic acids onto the active sites, complementary experiments were carried out to determine the effect of the presence of carboxylic acids on the reactivity of aldehyde function on the sulfide catalyst surface sites. All catalytic experiments were carried out in the presence of dimethyl disulfide added to the liquid feed in order to preserve the sulfided active sites.

Table 1
BET area, pore volume and chemical composition of the catalysts in their oxide form [25].

	Mo/Al_2O_3	$CoMo/Al_2O_3$	$NiMo/Al_2O_3$
BET area ($m^2\,g^{-1}$)	251	255	257
Pore volume ($cm^3\,g^{-1}$)	0.70	0.64	0.66
Mo (wt%)	9.9	9.2	9.3
Co (wt%)	–	4.2	–
Ni (wt%)	–	–	3.9

2. Experimental

2.1. Materials

The characteristics of commercial catalysts (Mo/Al_2O_3, $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$) were described in [25] and summarized in Table 1. Decanoic acid (98%) was purchased from SAFC, dodecanoic acid (98%), decanal (98%), 1-decanol (98%), 1-decanethiol (96%), 1-hexene (99%) and toluene (99.8%) were purchased from Sigma–Aldrich, n-heptane (99.7%) from Carlo Erba, and dimethyl disulfide (DMDS, 98%) from Fluka. They were used without further purification. H_2 (99.95%), 1% CO/H_2 (98% in CO) and 1% CO_2/H_2 (98% in CO_2) cylinders were provided by Air Liquide.

2.2. Catalytic tests

The particle size of the catalysts was in the range of 250–315 μm. The catalysts were diluted with carborundum to keep the volume of the catalyst bed constant. All the catalysts were sulfided in situ in a high-pressure dynamic flow reactor (length: 40 cm; inner diameter: 1.26 cm) using a solution of DMDS (5.8 wt%) in toluene. Under 4.0 MPa total pressure, the sulfiding mixture was injected at a starting temperature of 150 °C. After 1 h, the temperature was raised to 350 °C at a rate of 5 °C min^{-1} and it was maintained at this temperature for 14 h. The temperature of the reactor was then lowered to 340 °C, the reaction temperature.

The transformation of all reactants was carried out in the same fixed-bed reactor under 4 MPa of total pressure and 340 °C. The volume ratio H_2/feed was equal to 486.4 NL/L. The partial pressure of hydrogen was kept constant at 2.72 MPa. The reference model feed was composed of decanoic acid (7.8 wt%), DMDS (1.3 wt%) and n-heptane (2.6 wt%) diluted with toluene. Under these conditions (340 °C, 4 MPa), the initial partial pressures were 53 kPa of decanoic acid, 32 kPa of both H_2S and CH_4, 31 kPa of n-heptane (used as an internal standard for chromatography analysis) and 1.13 MPa of toluene. The deoxygenation of dodecanoic acid, decanal, 1-decanol and the desulfurization of 1-decanethiol were investigated under the same conditions. All experiments were performed during 7 h on stream.

In order to measure the impact of the presence of carboxylic acid on the deoxygenation of decanal, another set of experiments were performed for 12 h on stream by using successively: (i) a model feed containing decanal (7.1 wt%) as oxygenate (for 3 h on stream), (ii) a mixture containing both decanal (7.1 wt%) and dodecanoic acid (in the range of 0.2–3.4 wt%) as oxygenates (for 5 h on stream), (iii) the model feed used initially (for 4 h on stream). Besides oxygenated compounds, DMDS (1.3 wt%) was also added to the feeds. In these experiments, dodecanoic acid was used instead of decanoic acid since the products of the former did not overlap with the ones of decanal during the analytical measurements, allowing the determination of the decanal conversion. Obviously, the partial pressure of H_2 (2.72 MPa) was kept constant by changing the quantity of toluene (between 85.6 and 88.9 wt%) in the several model feeds used.

2.3. Activity measurements

The reactor effluents were collected at 10 °C (using a Minichiller-Huber cryostat). The liquid samples, obtained after drying over MgSO$_4$, were periodically analyzed on a Varian 430 chromatograph equipped with a DB1 capillary column (length: 30 m; inside diameter: 0.320 mm; film thickness: 5 μm) and a flame ionization detector. For a better determination of the conversion of acid, the samples were silylated prior to their chromatographic analysis, using N,O-bis(trimethylsilyl)trifluoroacetamide with 1% of chlorotrimethylsilane (BSTFA-TMCS 99:1, provided by Supelco) as the silylation agent. The reaction products were identified by GC/MS analysis using either a 1200 TQ mass spectrometer coupled with a Varian 3800 chromatograph or an Agilent 7200 Series Q-TOF-GC/MS System coupled with an Agilent 7890A chromatograph) and also by adding aliquots of commercial compounds.

Gaseous effluents (CO, CO$_2$, H$_2$S and CH$_4$) were quantified online by using Varian 450 chromatograph equipped with an automatic sampling valve, two HayeSep Q columns (length: 0.5 m; inside diameter: 1/8 in; film thickness: 2.0 mm), a 13× molecular sieve (length: 1.5 m; inside diameter: 1/8 in; film thickness: 2.0 mm) and a thermal conductivity detector. A backflush procedure allowed to remove organic compounds.

For each catalyst and reactant, different conversions were obtained by changing the contact time using independent experiments. The contact time (in min) is defined as the ratio between the volume of the catalyst and the gas flow of the oxygenated reactant.

Assuming a first order reaction, the total activity of each catalyst was calculated according to the following equation:

$$A = -\frac{F}{w_{cat}}\mathrm{Ln}(1 - X)$$

where A is the global activity (in mol h^{-1} g^{-1}), F is the molar flow of the oxygenated reactant (in mol h^{-1}), w_{cat} the weight of the catalyst (in g), X is the conversion of decanoic acid measured after 7 h on stream (in the range of 25–35%).

3. Results and discussion

3.1. Transformation of decanoic acid over Mo/Al$_2$O$_3$

During the transformation of decanoic acid without catalyst at 340 °C under 4 MPa, decanal was detected as traces (less than 1 mol%). Under the same operating conditions, the unpromoted sulfided Mo/Al$_2$O$_3$ catalyst was quite stable in this reaction: its residual activity was equal to 93% after 7 h on stream (contact time used equal to 0.17 min). Three types of products were identified: oxygenated molecules, sulfur-containing products and deoxygenated hydrocarbons (Table 2 and Fig. 1). Decanal and 1-decanol were the main oxygenated compounds. Decyl decanoate formed by esterification reaction of 1-decanol and decanoic acid was also detected. Esterification of heptanoic acid was reported to occur over supported [38] and unsupported [41] sulfided catalysts. The acidic properties of the support and/or the sulfide phase are probably responsible for such a reaction since esterification is an acid-catalyzed reaction. Traces of didecyl ether were also detected, resulting from the condensation between two molecules of 1-decanol. The oxygenated products appeared as the main products of decanoic acid at contact times below 0.3 min, corresponding to conversions lower than 40%. At higher contact times, their quantity decreased since these products were intermediates.

Sulfur-containing compounds appeared also to be intermediates formed in lower amounts compared to the oxygenated products (Fig. 1 and Table 2). At low contact times, the main sulfur-containing product was methylthiodecanoate, whereas 1-decanethiol was the major product at contact time of 0.2 min. The

Table 2
Transformation of oxygenated (decanoic acid, decanal and 1-decanol) compounds and a sulfur-containing compound (1-decanethiol) over Mo/Al$_2$O$_3$ at 340 °C under 4 MPa of total pressure at 0.17 min as contact time.
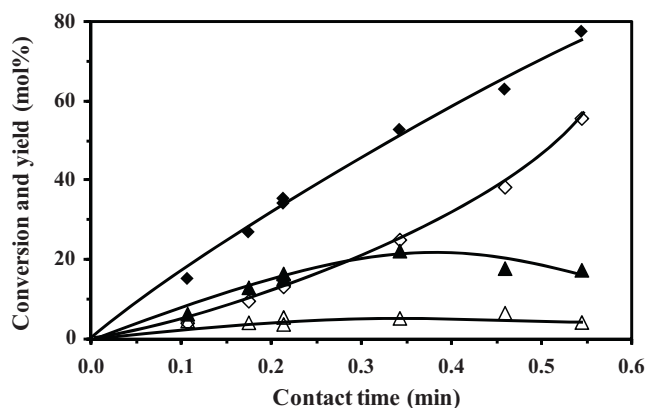
Reactant	Conv (%)	Yield in deoxygenated products (mol%)	Product distribution (mol%)								
			Decanal	1-Decanol	1-Decanethiol	Decyl decanoate	Decenes	Decane	Nonenes	Nonane	Other products
Decanoic acid	27.1	9.7	22.8	18.6	5.7	6.9	9.6	12.3	8.2	5.7	10.2[a]
Decanal	92.8	67.3	–	16.4	5.0	0	44.4	24.4	0	3.7	6.1[b]
1-Decanol	83.6	76.9	0.5	–	2.2	0	58.4	33.5	0	0	5.4[c]
1-Decanethiol	97.0	93.4	0	0	–	0	39.1	57.2	0	0	3.7[d]

a Decylmethyl sulfide (1.7 mol%); nonylmethyl sulfide (0.7 mol%); 1-nonanethiol (1.8 mol%); methylthiodecanoate (C$_9$H$_{19}$COSCH$_3$; 5.9 mol%); didecyl ether (0.1 mol%).
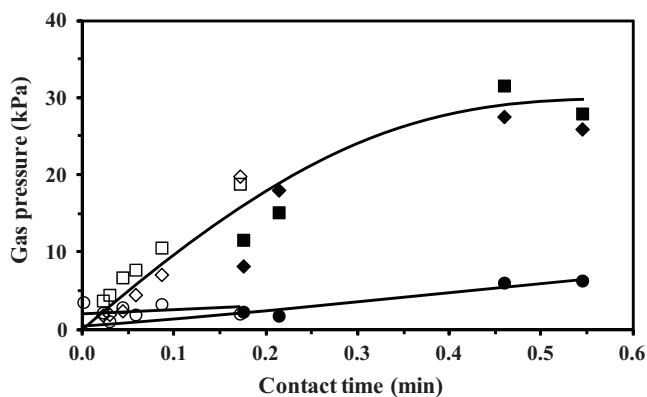b Decylmethyl sulfide (3.4 mol%); didecyl ether (2.7 mol%).
c Decylmethyl sulfide (3.9 mol%); didecyl ether (1.5 mol%).
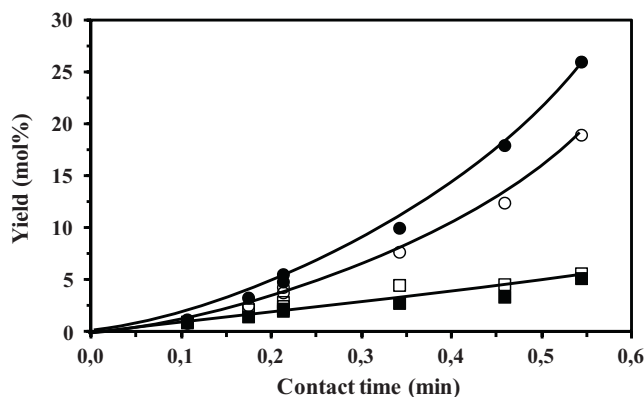d Decylmethyl sulfide (3.7 mol%).

Fig. 1. Effect of contact time on the transformation of decanoic acid over Mo/Al$_2$O$_3$ (340 °C, 4 MPa). Conversion of decanoic acid (♦); yield in oxygenated products (decanal, 1-decanol, decyl decanoate, didecyl ether:▲); yield in sulfur-containing products (1-decanethiol, decylmethyl sulfide, nonylmethyl sulfide, 1-nonanethiol, methylthiodecanoate: △); yield in deoxygenated products (nonane, nonenes, decane, decenes: ◇).

formation of these products can be explained by the fact that DMDS was added to the liquid feed in order to maintain the sulfidation state of the catalyst. Under operating conditions, DMDS was never observed in the liquid samples due to its high reactivity. Indeed, DMDS was completely decomposed into methanethiol at the first step and then into CH$_4$ and H$_2$S as ultimate products, as reported by Texier et al. [45]. Fig. 2 shows that the expected values of H$_2$S and CH$_4$ (32 kPa of each compound), corresponding to the total decomposition of DMDS into both compounds, were only obtained at contact times higher than 0.4 min. At lower contact times, methanethiol was detected in the liquid samples but not quantified. The presence of methanethiol can explain the formation of sulfur-containing products such as methylthiodecanoate, decylmethyl sulfide and nonylmethyl sulfide. As indicated in Table 2, these compounds represented 8.3 mol% of all the products obtained at the decanoic acid conversion of 27%. Obviously, the use of H$_2$S as sulfiding agent instead of DMDS would prevent the formation of such sulfur-containing compounds. At higher conversions, i.e. at higher contact time values, their quantities became very low since the decomposition of DMDS into CH$_4$ and H$_2$S was practically total, as shown in Fig. 2. In addition, the presence of H$_2$S in the reaction medium can explain the formation of sulfur-containing products such as 1-decanethiol. Indeed, 1-heptanethiol was detected as a reaction product in the transformation of heptanoic acid over sulfided catalysts [38–40].
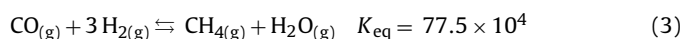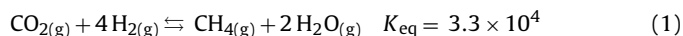

Fig. 2. Effect of contact time on the quantity of CH$_4$ (□; ■), CO (○; ●) and H$_2$S (◇; ♦) measured during the transformation of decanoic acid (full symbols) and decanal (empty symbols) over Mo/Al$_2$O$_3$ (340 °C, 4 MPa).

Fig. 3. Effect of contact time on the yield in deoxygenated products obtained from the transformation of decanoic acid over Mo/Al$_2$O$_3$ (340 °C, 4 MPa). Decane (●); decenes (○); nonane (■); and nonenes (□).
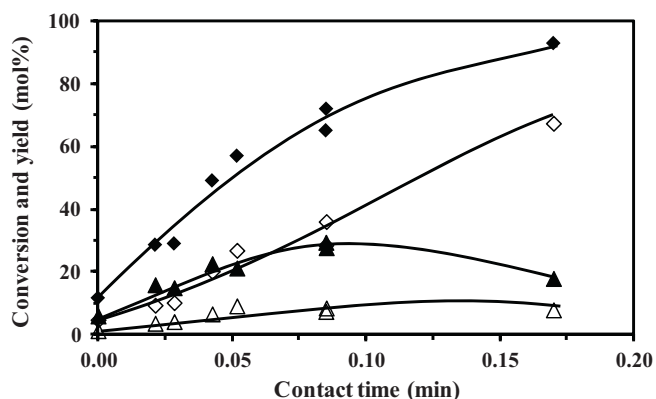
Deoxygenated compounds were the main products when conversion was higher than 40%. Decane and decenes were observed in larger quantities than nonane and nonenes (Fig. 3). Five isomers of decenes were detected, but only 1-decene was formally identified as the main isomer of decenes. Whatever the contact time and hence the conversion, the decane/decenes ratio was about the same (close to 1.3), indicating that decane was not obtained by hydrogenation of decenes over Mo/Al$_2$O$_3$. The same conclusion can be made concerning the C9 hydrocarbons since the nonane/nonenes ratio was close to 0.8 whatever the conversion of decanoic acid. To verify the reactivity of alkenes in the presence or absence of carboxylic acid, additional experiments were performed. In the first experiment, the mixture containing 1-hexene (0.2 wt%), DMDS (1.3 wt%), n-heptane (2.6 wt%) and toluene (88.1 wt%) was treated in presence of decanoic acid (7.8 wt%), under the same operating conditions (Mo/Al$_2$O$_3$, 340 °C and 4 MPa). This experiment showed that 1-hexene was basically unreactive since only 2.5 mol% of its isomers and traces of hexane (less than 1 mol%) were observed. In the second experiment, i.e. without decanoic acid in the liquid feed, isomers of hexene (52 mol% of yield) and hexane (22 mol% of yield) were obtained. These results showed that the hydrogenation of alkenes is possible over Mo/Al$_2$O$_3$, but significantly inhibited by carboxylic acid.

In addition to the organic products described above, light gaseous compounds (CH$_4$, H$_2$S and CO) were also detected during the transformation of the carboxylic acid, and their quantities depended on the contact time (Fig. 2). Interestingly, CO$_2$ was never observed as a gas product of the transformation of decanoic acid, which is in agreement with the results reported by Philippe et al. [20]. Two explanations for this fact can be proposed: (i) CO$_2$ was not produced during the transformation of decanoic acid and therefore no decarboxylation of carboxylic acid occurred, (ii) CO$_2$ was formed and after it was completely converted into CH$_4$ by methanation (Eq. (1)) and/or into CO by the reverse water-gas shift reaction (Eq. (2)). Thermodynamic calculations using the HSC chemsistry® software [46] indicate that the latter reaction (Eq. (2)) is thermodynamically disfavoured under our experimental conditions.

$$CO_{2(g)} + 4H_{2(g)} \leftrightarrows CH_{4(g)} + 2H_2O_{(g)} \quad K_{eq} = 3.3 \times 10^4 \quad (1)$$

$$CO_{2(g)} + H_{2(g)} \leftrightarrows CO_{(g)} + H_2O_{(g)} \quad K_{eq} = 4.2 \times 10^{-2} \quad (2)$$

$$CO_{(g)} + 3H_{2(g)} \leftrightarrows CH_{4(g)} + H_2O_{(g)} \quad K_{eq} = 77.5 \times 10^4 \quad (3)$$

In order to verify the reactivity of CO$_2$, additional experiment was performed. For this purpose, the reactivity of CO$_2$ was measured by its introduction to the reactor at 10 kPa during the
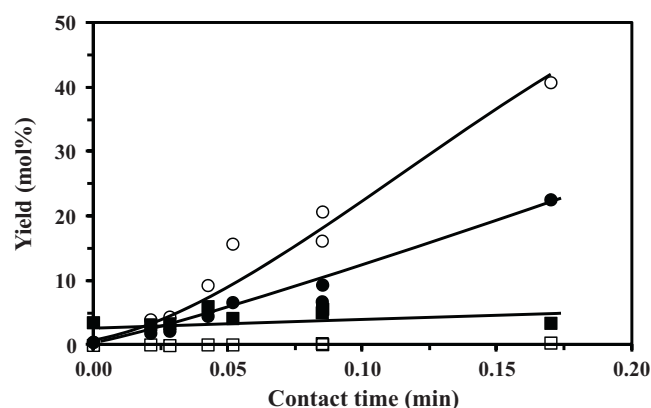
Fig. 4. Effect of contact time on the transformation of decanal over Mo/Al$_2$O$_3$ (340 °C, 4 MPa). Conversion of decanal (♦); yield in oxygenated products (1-decanol, decyl decanoate, didecyl ether: ▲); yield in sulfur-containing products (1-decanethiol, decylmethyl sulfide, nonylmethyl sulfide, 1-nonanethiol: △); yield in deoxygenated products (nonane, nonenes, decane, decenes: ◊).

deoxygenation of decanoic acid over Mo/Al$_2$O$_3$. Under these conditions, the same partial pressure of CO$_2$ was detected in the outlet gas stream of the reactor indicating that CO$_2$ did not react with H$_2$, that led to the conclusion that decarboxylation of decanoic acid did not occur. Consequently, the C9 hydrocarbons (nonenes and nonane) were only obtained by decarbonylation from either decanoic acid and/or decanal. In addition, for each experiment, CO was produced in the same quantities as nonane and nonenes, indicating that no conversion of CO into CH$_4$ (Eq. (3)) occurred, which is in agreement with the results reported in [27].

3.2. Transformation of decanal and its main intermediates (1-decanethiol and 1-decanol) over Mo/Al$_2$O$_3$

In order to have a deeper insight into the scheme of the deoxygenation of decanoic acid, the transformation of decanal and its main intermediates (1-decanethiol and 1-decanol) was also studied over Mo/Al$_2$O$_3$ (340 °C, 4 MPa). As shown in Fig. 4, the conversion of decanal was low (close to 11%) without catalyst, giving mainly 1-decanol (4.6 mol%) and nonane (3.6 mol%). As expected, Mo/Al$_2$O$_3$ favoured the transformation of decanal into deoxygenated products. The C10 hydrocarbons (decane and decenes) were the main deoxygenated products (Fig. 5). As the decane/decenes ratio was close to 0.5, whatever the contact time, it can be concluded that hydrogenation of decenes into decane did not occur, which is in agreement with the results already reported, i.e. when decanoic

Fig. 5. Effect of contact time on the yield in deoxygenated products obtained from the transformation of decanal over Mo/Al$_2$O$_3$ (340 °C, 4 MPa). Decane (●); decenes (○); nonane (■); nonenes (□).

Table 3
Transformation of 1-decanol and 1-decanethiol over Mo/Al$_2$O$_3$ at 340 °C under 4 MPa of total pressure.

Reactant	Contact time (min)	Conversion (%)	Decane/decenes ratio
1-Decanol	0.02	21	0.3
	0.17	77	0.6
1-Decanethiol	0.02	40	0.8
	0.17	97	1.5

acid was used as reactant. Moreover, this ratio was lower than the one measured starting from the carboxylic acid (close to 1.3). This result probably indicates that the formation of decenes from decanal could be inhibited by decanoic acid.
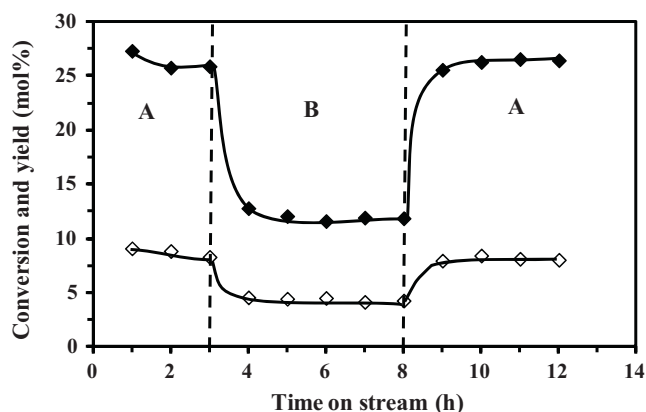
The isomers of nonene were detected only as traces and the yield of nonane was independent of the contact time and equal to the one measured without catalyst (Fig. 5). Therefore, nonane was only produced by a non-catalyzed decomposition of decanal. For this reason, the partial pressure of CO which was generated by the thermal decarbonylation of decanal was always constant (near 2 kPa), as indicated in Fig. 2. This result is in agreement with DFT calculations showing that the decarbonylation of propanal over sulfide MoS$_2$ phase was unlikely due to a high energy barrier [41].

The reactivity of both intermediates (1-decanol and 1-decanethiol) was also investigated over Mo/Al$_2$O$_3$ under the same experimental conditions in presence of DMDS in the liquid feed. As shown in Table 3, 1-decanethiol was more reactive than 1-decanol since the conversion of the former was always higher than that of the alcohol. Whatever the contact time, both compounds mainly led to the formation of decenes and decane. Nevertheless, the decane/decenes ratio depended on both reactant and contact time: this ratio was always higher when 1-decanethiol was used as reactant and it increased with contact time whatever the reactant (Table 3). It can be concluded that (i) the direct formation of alkane seems favoured starting from a thiol instead of starting from an alcohol; (ii) the hydrogenation of decenes into decane occurred in absence of both decanoic acid and decanal in the reaction medium.

3.3. Effect of a carboxylic acid on the transformation of decanal over Mo/Al$_2$O$_3$

Decanal was at least 3 times more reactive than decanoic acid over Mo/Al$_2$O$_3$ (Table 2), that may result from an inhibiting effect of carboxylic acid on the transformation rate of aldehyde. In order to demonstrate such an inhibiting effect, transient experiments were performed using successively two model feeds containing as oxygenates either decanal alone or decanal and dodecanoic acid in mixture. Dodecanoic acid was used instead of decanoic acid in order to precisely quantify the conversion of decanal. Previously, it was verified that both carboxylic acids (decanoic and dodecanoic acids) had the same reactivity.

As an example, Fig. 6 shows the effect of the presence of 1.8 wt% of dodecanoic acid, corresponding to 10.4 kPa as a partial pressure of carboxylic acid, on the conversion of decanal. For such an experiment, the model feed containing both oxygenates was introduced after 3 h of the feed containing only decanal as oxygenate. Finally, dodecanoic acid was removed from the model feed and then the experiment was carried out and left under the initial conditions for 4 h. An inhibiting effect of dodecanoic acid on the transformation of decanal was clearly highlighted (Fig. 6). Indeed, a fast decrease of the decanal conversion in the presence of the carboxylic acid was observed: its conversion was 26% without dodecanoic acid and dropped to 12% in presence of 10.4 kPa of dodecanoic acid. It can be noticed that products resulting from the transformation of dodecanoic acid were only observed as traces, since its conversion
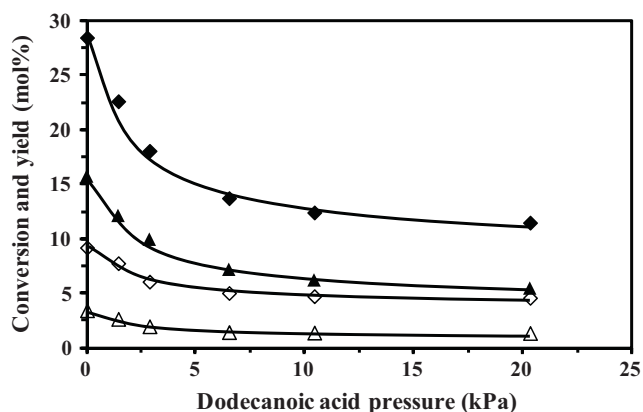
Fig. 6. Effect of time on stream on the conversion of decanal (♦) and in the yield in deoxygenated products (◊) over Mo/Al$_2$O$_3$ (340 °C, 4 MPa, 0.02 min as contact time) using a transient experiment: in absence (before 3 h and after 8 h: A) and in presence of dodecanoic acid (1.8 wt%, between 3 h and 8 h: B).
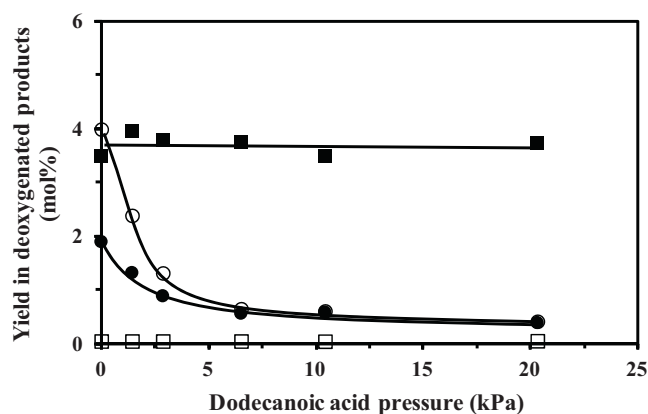
was less than 5% for this value of contact time (0.02 min). Finally, the decanal conversion reached the same value obtained when the reaction was run from the beginning without carboxylic acid, showing that the inhibition of the carboxylic acid was totally reversible. Consequently, such a total reversible inhibition can be explained by a competitive adsorption between the carboxylic acid and the alde-hyde onto the active sites of the catalyst, in favour of the carboxylic acid. This assumption is in good agreement with the DFT study reported by Dupont et al. [47] showing a stronger adsorption of propanoic acid ($-63 \, kJ \, mol^{-1}$) than that of propanal ($-37 \, kJ \, mol^{-1}$) over a MoS$_2$ phase. It can be noticed that a significant inhibiting effect of decanoic acid attributed to its strong adsorption on active sites was also observed on the desulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene over a CoMoP/Al$_2$O$_3$ catalyst [20].

Such experiments were carried out in the presence of different amounts of dodecanoic acid (between 0.2 and 3.4 wt% which correspond to partial pressures in the range of 1.4 and 20.3 kPa). Increasing the content of carboxylic acid resulted in a decrease of the conversion of decanal (Fig. 7). As expected, the total kinetic order with respect to dodecanoic acid was negative and equal to -0.26.

Fig. 8 shows the effect of the partial pressure of the carboxylic acid on the yield of hydrocarbons. The yield in nonane was not

Fig. 7. Effect of dodecanoic acid partial pressure on the transformation of decanal over Mo/Al$_2$O$_3$ (340 °C, 4 MPa, 0.02 min as contact time). Conversion of decanal (♦); yield in oxygenated products (1-decanol, decyl decanoate, didecyl ether: ▲); yield in sulfur-containing products (1-decanethiol, decylmethyl sulfide, nonylmethyl sulfide, 1-nonanethiol: △); yield in deoxygenated products (nonane, nonenes, decane, decenes: ◊).

Fig. 8. Effect of dodecanoic acid partial pressure on the yield in deoxygenated products obtained from the transformation of decanal over Mo/Al$_2$O$_3$ (340 °C, 4 MPa, 0.02 min as contact time). Decane (●); decenes (○); nonane (■); and nonenes (□).
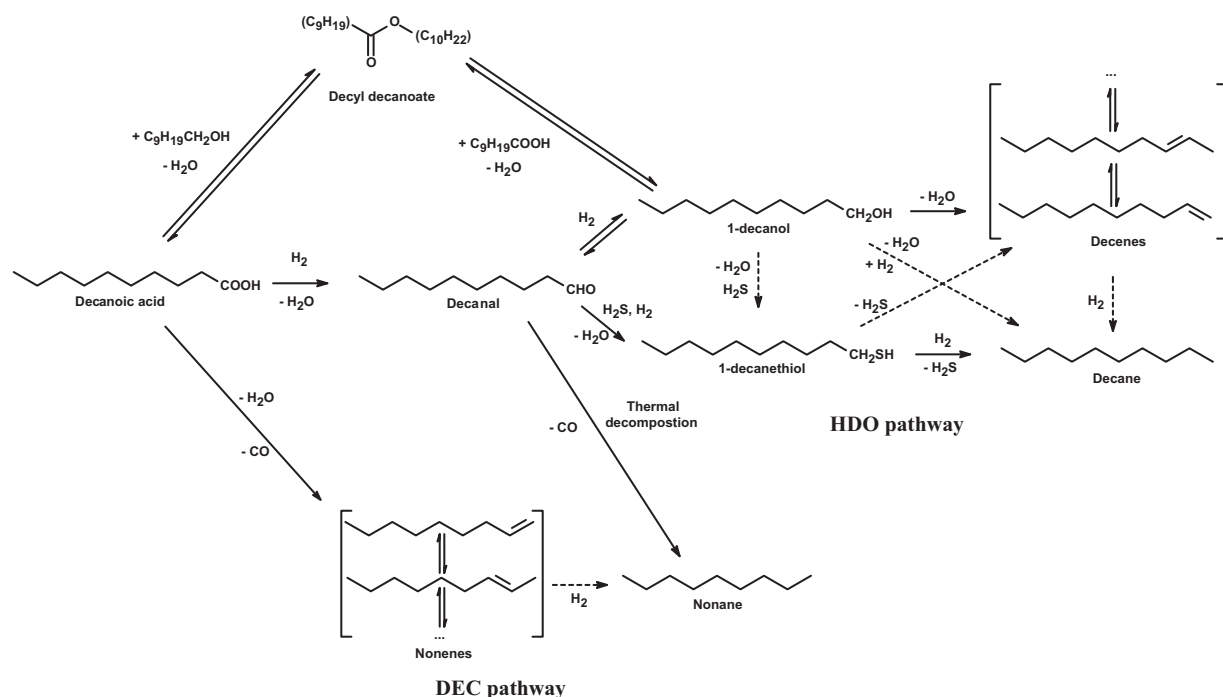
modified by dodecanoic acid since this alkane was obtained only by a non-catalyzed reaction, as discussed before. In addition, it was observed that the formation of the isomers of decene was more inhibited by dodecanoic acid than the formation of decane. Indeed, the decane/decenes ratio was equal to 0.5 without dode-canoic acid and this ratio increased to 1 with increasing the quantity of dodecanoic acid introduced into the model feed. This result is in agreement with the fact that the decane/decenes ratio determined in the case of the use of decanoic acid as reactant differs from that measured starting from decanal over Mo/Al$_2$O$_3$. This implies that the selectivity of the unpromoted catalyst for the decanal trans-formation appears to be modified in the presence of carboxylic acid.

3.4. Reaction scheme and plausible mechanisms for the deoxygenation of decanoic acid over Mo/Al$_2$O$_3$

The data collected from experiments on the transformation of decanoic acid and its main intermediates (decanal, 1-decanol and 1-decanethiol) are very helpful in shedding light on the reaction pathways of the deoxygenation of carboxylic acid into hydrocar-bons. Thus, the reaction scheme of the transformation of decanoic acid over sulfide catalyst is depicted in Scheme 1. It should be noted that the products containing methylthio-group (methylth-iodecanoate, decylmethyl sulfide and nonylmethyl sulfide) which were obtained in small amounts, are not included in Scheme 1.

The deoxygenation of decanoic acid involves two main pathways: the hydrodeoxygenation (HDO) route and the decar-bonylation (DEC) route. Concerning the HDO pathway, its first step requires the hydrogenation of decanoic acid followed by a dehydra-tion reaction leading to decanal, the main oxygenated intermediate at low conversion, water being a by-product. Based on our exper-imental results, decanal probably reacts by three parallel routes leading to decane, decenes and nonane as hydrocarbons. The main route of its transformation leads firstly to 1-decanol by hydrogena-tion. Then, this alcohol can be deoxygenated by an elimination reaction yielding 1-decene and water. Decane was also observed as a product even at low conversion of 1-decanol (Table 3), show-ing that the hydrogenolysis of the alcohol into alkane cannot be ruled out. In addition, 1-decene can undergo isomerization by dou-ble bond shift leading to four isomers, which are probably cis/trans 2- and 3-decenes. It is also important to note that the hydrogena-tion of the decene isomers into decane did not occur over Mo/Al$_2$O$_3$ in presence of decanoic acid and/or decanal.

The second route of the transformation of decanal could involve the formation of 1-decanethiol as an intermediate. The

Decyl decanoate (C_9H_{19}) O $(C_{10}H_{22})$

$+ C_9H_{19}CH_2OH$ $- H_2O$

$+ C_9H_{19}COOH$ $- H_2O$

Decanoic acid COOH H_2 $- H_2O$ Decanal CHO

H_2

H_2S, H_2 $- H_2O$

1-decanol CH$_2$OH $- H_2O$ Decenes

$- H_2O$ H_2S

$- H_2O$ $+ H_2$

$- H_2S$

1-decanethiol CH$_2$SH H_2 $- H_2S$ Decane

H_2

HDO pathway

$- H_2O$

$- CO$

Thermal decompostion $- CO$

Nonenes H_2 Nonane

DEC pathway

Scheme 1. Reaction network of the deoxygenation of decanoic acid over sulfide catalyst.

formation of 1-decanethiol from decenes by addition of a sulfhydryl group is highly improbable. Indeed, over Mo/Al$_2$O$_3$ in presence of DMDS in the liquid feed, sulfur-containing products were never observed from 1-hexene. Similarly, no sulfur-containing products were described starting from olefins as reactants over sulfided catalysts [48]. Dupont et al. [47] proposed that the deoxygenation of propanol was activated by sulfhydryl groups, present on the sulfide phase, through a nucleophilic substitution mechanism, allowing the formation of propanethiol. Nevertheless, the authors reported a very high activation barrier (about 130 kJ mol^{-1}) for such a mechanism. In our experimental conditions, the yield of 1-decanethiol remained very low (equal to 1.2 mol%) whatever the conversion of 1-decanol. Therefore, the formation of 1-decanethiol by a nucleophilic substitution reaction of 1-decanol appears very unlikely. However, as 1-decanethiol was found more reactive than 1-decanol over unpromoted sulfide catalyst (Table 3), such a reaction cannot be ruled out. A direct formation of 1-decanethiol starting from decanal could be possible, as depicted in Scheme 1.

As indicated in Table 3, the reactivity of 1-decanol was different than that of 1-decanethiol. It can be considered that alcohol reacts mainly by dehydration leading to an alkene, as discussed above, whereas 1-decanethiol could be transformed mainly into alkane. Indeed, a DFT study showed that the hydrogenolysis of ethanethiol into ethane was more favourable compared to the elimination reaction leading to ethene [49]. This assumption could explain why the decane/decenes ratio significantly depends on the reactant used as discussed before. Thus, when decanal was used as a reactant, the decane/decenes ratio was lower than 1, indicating that the main route of its deoxygenation involved dehydration of 1-decanol. In presence of both carboxylic acids (decanoic and dodecanoic acids), this ratio was higher and close to 1. This fact can be explained by a significant inhibition of the hydrogenation of decanal into 1-decanol due to the presence of carboxylic acid, the direct desulfuration of 1-decanethiol into decane hence became the main route of the deoxygenation of decanal.

The third route of the deoxygenation of decanal leading to nonane is a non-catalyzed reaction. Obviously, the quantity of nonane was not included in the HDO route.

The second deoxygenation route of decanoic acid, called the DEC pathway, led only to the nonene isomers over Mo/Al$_2$O$_3$, since alkenes were not hydrogenated into alkane over this kind of catalyst. This route involves both dehydration and decarbonylation reactions of decanoic acid leading to 1-nonene as the primary hydrocarbon product, the oxygenated by-products being H$_2$O and CO. This alkene can also be isomerized by double bond shift, leading to several nonene isomers.

It is now well accepted that the nature of active sites present on the edges of the MoS$_2$ phase in sulfided catalysts is a sulfur vacancy schematically represented in Scheme 2. The first step of the proposed reaction mechanism requires the heterolytic dissociation of molecular hydrogen to a metal hydride (Mo–H) and a sulfhydryl (—SH) group as proposed by Sun et al. [50]. Then, adsorption of decanoic acid through its carbonyl group can occur on a sulfur vacancy, in agreement with the theoretical study reported by Dupont et al. [47]. The next step could be a protonation of decanoic acid due to the acidity of the SH group. After elimination of water, the adsorbed carbocation could be a key intermediate. Indeed, we assume that this cationic species could be a common intermediate for the DEC and the HDO pathways. This intermediate can undergo either a hydride addition step or an elimination step. In the first case, the direct addition of a hydride species to the cationic intermediate leading to decanal, which is the primary product formed by the HDO route. In the second case, the C—C bond breaking might occur through a basic attack on the hydrogen atom in β-position with respect to the carbon atom carrying the positive charge of the cationic intermediate. The basic site could be a sulfur anion (S^{2-}) species neighbouring of the sulfur vacancy as proposed in [51]. Over the unpromoted catalyst, the transformation of decanoic acid was mainly done through the HDO pathway since the HDO/DEC selectivity was equal to 4.2 (Table 4). Consequently, it can be assumed that the addition step from the cationic intermediate adsorbed onto an unpromoted sulfur vacancy involving a hydride species, as depicted in Scheme 3a, is much easier than the elimination step involving a basic site.
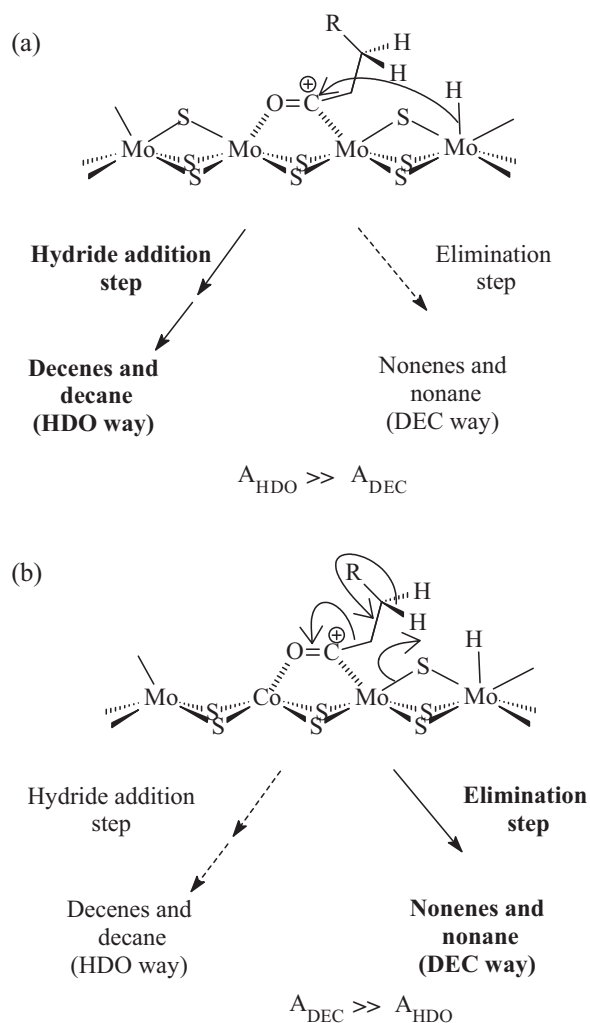
Scheme 2. Proposition of a catalytic cycle involved during the transformation of decanoic acid on a schematic unpromoted active site.

3.5. Transformation of decanoic acid and decanal over $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$: effect of promoters

The reactivity of decanoic acid was also evaluated over both promoted catalysts ($CoMo/Al_2O_3$ and $NiMo/Al_2O_3$) at 340 °C under 4 MPa, in presence of DMDS. Whatever the contact time, DMDS was totally converted into CH_4 and H_2S under these conditions. Consequently, 1-decanethiol was only observed as sulfur-containing product. Table 4 shows that the total activity of both promoted catalysts was slightly higher than that of Mo/Al_2O_3. Then, the global promoting effect of Co and Ni, measured as the ratio between the activity of promoted catalysts and the unpromoted catalyst, was 1.3 and 1.5 for Co and Ni, respectively. These promoting effects were in the same range as those reported for the transformation of 2-ethylphenol over the same sulfided catalysts: 2.3 for Co and 2.0 for Ni [27]. Moreover, 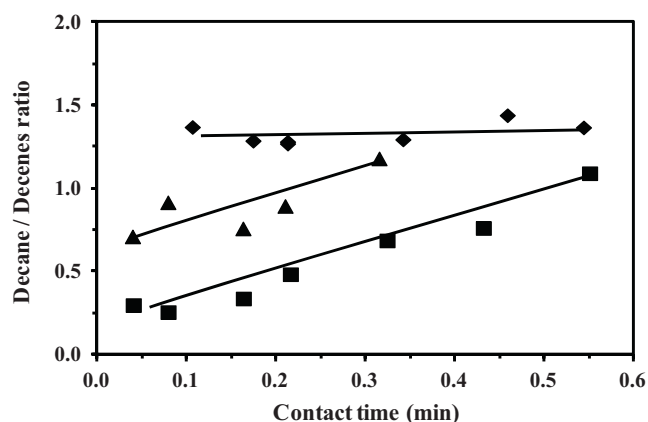both promoted catalysts were much more active in deoxygenation than the unpromoted catalyst. Indeed, in the same range of conversion of decanoic acid (27–37%) both promoted catalysts led to more than 90 mol% of deoxygenated products, whereas the unpromoted catalyst yielded only 36 mol% of deoxygenated products (Table 4). These results are in good agreement with the fact that Co and Ni are known for weakening the metal–sulfur bond and hence increasing the number of sulfur vacancies considered as active sites for deoxygenation reactions.

The relative importance of each deoxygenation route was very dependent on the catalyst. Indeed, a strong promoting effect of Co and Ni on the DEC route was highlighted, ranging from 5.5 for Co to 6.6 for Ni (Table 4). On the opposite, the HDO route was clearly inhibited by Ni and Co, since the HDO activity of both promoted catalysts was practically halved compared to the HDO activity of the unpromoted catalyst. Consequently, the HDO/DEC selectivity was very dependent on the catalyst and was the lowest over $NiMo/Al_2O_3$ (close to 0.3) and the highest over Mo/Al_2O_3 (equal to 4.2). As a result, the C9 hydrocarbons (nonane and nonenes), which were obtained by the DEC route, were the main deoxygenated products of decanoic acid over both promoted catalysts, in accordance with the selectivity of the deoxygenation of decanoic acid measured over $CoMoP/Al_2O_3$ [20] and $NiMo/Al_2O_3$ [37]. In the case of both promoted catalysts, alkenes (nonenes and decenes) were hydrogenated into alkane (nonane and decane), since the decane/decenes ratio increased with the augmentation of the contact time (Fig. 9). The same trend was observed for the nonane/nonenes ratio. This is in agreement with the fact that a promoting effect of Co and Ni on the hydrogenation of various olefins was already reported in [52]. This, however, makes it difficult to carry out a precise quantification of the amount of nonane arising from the non-catalyzed decomposition of decanal and the quantity of nonane coming from hydrogenation of the nonene isomers. The DEC route of all sulfided catalysts that includes the direct decarbonylation of decanoic acid, was therefore slightly overestimated, particularly in the case of Mo/Al_2O_3, since the quantity of nonane formed was taken into account in the calculation of the DEC activity of all catalysts.

Table 4
Activity and selectivity of sulfided Mo-based catalysts for the transformation of decanoic acid at 340 °C under 4 MPa of total pressure. Promoting effects of Ni and Co are given in brackets (defined as the ratio between the activity of promoted catalysts and the unpromoted catalyst).

	Mo/Al_2O_3	$CoMo/Al_2O_3$	$NiMo/Al_2O_3$
Activity (mmol g^{-1} h^{-1})			
Total	145	189(1.3)	212(1.5)
HDO	102	52(0.5)	50(0.5)
DEC	24	133(5.5)	159(6.6)
Other[a]	19	4(0.2)	3(0.2)
HDO/DEC selectivity	4.2	0.4	0.3
Selectivity in hydrocarbons (mol%)[b]	36	90	92
C10/C9 hydrocarbons ratio[c]	1.6	0.3	0.2

[a] Activity in formation of decyl dodecanoate, didecyl ether and methylthiodecanoate.
[b] Selectivity in nonane, nonenes, decane and decenes measured at iso-conversion (near 30%).
[c] (decane + decenes)/(nonane + nonenes) ratio determined at iso-conversion (near 30%).

Scheme 3. Description of the elementary steps being likely to occur from the cationic intermediate adsorbed: hydride addition in the cationic intermediate adsorbed onto a schematic unpromoted site (a); elimination step involving a schematic Co-promoted site (b). Such sites were described in [27].

Table 5
Partial pressures of gaseous compounds measured during the transformation of decanoic acid over promoted sulfided catalysts (0.32 min as contact time, 340 °C, 4 MPa of total pressure).

	Partial pressure (kPa)			
	CO_2	CO	CH_4	H_2S
CoMo/Al$_2$O$_3$	0	19.9	30.2	28.0
NiMo/Al$_2$O$_3$	0	22.1	32.7	30.8

As an example, the partial pressures of gaseous compounds detected during the transformation of the model feed, containing decanoic acid and DMDS, over both promoted catalysts at a contact time of 0.32 min are given in Table 5. As observed over the unpromoted catalyst, CO_2 was never detected indicating that decarboxylation of decanoic acid did not occur over promoted catalysts. Indeed, it was experimentally verified that CO_2 was not reactive over both promoted catalysts, as previously demonstrated for the Mo/Al$_2$O$_3$ catalyst. The quantity of CO, generated by decarbonylation of decanoic acid, was higher over NiMo/Al$_2$O$_3$ than over CoMo/Al$_2$O$_3$, in agreement with the higher activity of the former catalyst in decarbonylation (DEC activity), as indicated in Table 4. In addition, both CH_4 and H_2S partial pressures were close to the expected values (32 kPa) for both promoted catalysts, since the decomposition of DMDS into CH_4 and H_2S was total over these catalysts.

It is now well admitted that the most stable position of Co or Ni atoms is in substitution of Mo on the edges of the sulfided phase which leading to the Co(Ni)-Mo-S phase [53–56]. It was proposed that Co and Ni allows an increase of the electron density on the sulfur atoms of the sulfided phase [57], the sulfur anions neighbouring of the promoters could be therefore more basic than those of the unpromoted phase [51,58,59]. This could explain the strong promoting effect of Co and Ni on the DEC route. Indeed, the elimination step, depicted in Scheme 3b, occurs through a β-elimination process involving a sulfur anion acting as a basic site. This type of mechanism was also proposed to explain the C–S bond scission occurring during the direct desulfurization way of dibenzothiophene compounds, which was the main desulfurization route of dibenzothiophene over promoted sulfided catalysts [59].

Furthermore, a correlation between the quantity of nickel in bulk Ni$_3$S$_2$ and the decarbonylation/decarboxylation of heptanoic acid (yielding C6 hydrocarbons) was highlighted over unsupported Ni-promoted MoS$_2$ catalysts [41]. These bulk species (Co$_9$S$_8$ or Ni$_3$S$_2$) can also be present when sulfide phase was supported on alumina [60], but in lower quantities than the promoted Co(Ni)-Mo-S phase as deduced from XPS analysis [61,62]. Consequently, the involvement of Co$_9$S$_8$ and Ni$_3$S$_2$ clusters, present on supported catalysts, as active sites to explain a part of the promoting effect of the DEC way cannot be ruled out, even if their morphology (and hence their activity) is probably very different from those of unsupported sulfide phase.

It is also worth noting that the differences in activity and selectivity between Mo/Al$_2$O$_3$ and NiMo/Al$_2$O$_3$ measured either starting from a renewable raw material (a rapeseed oil: reported in [33]) or using decanoic acid as a model reactant (this work) are similar, showing that carboxylic acids are key intermediates of the deoxygenation of vegetable oils and decanoic acid is a good oxygenated molecule to model the deoxygenation of this kind of material.

A promoting effect of cobalt was also highlighted for the transformation of decanal, since CoMo/Al$_2$O$_3$ was approximately twice as active as Mo/Al$_2$O$_3$, the proportion of hydrocarbons totally deoxygenated being higher over the promoted catalyst (Table 6). Indeed, the decene isomers were the main products over CoMo/Al$_2$O$_3$ whereas 1-decanol was favoured over Mo/Al$_2$O$_3$ for this contact time (0.02 min). The decane/decenes ratio depended

Fig. 9. Effect of the contact time on the decane/decenes ratio obtained from the deoxygenation of decanoic acid (340 °C, 4 MPa). Mo/Al$_2$O$_3$ (♦); CoMo/Al$_2$O$_3$ (■); and NiMo/Al$_2$O$_3$ (▲).

Table 6
Transformation of decanal over Mo/Al$_2$O$_3$ and CoMo/Al$_2$O$_3$ (0.02 min as contact time, 340 °C, 4 MPa of total pressure).

	Conv (%)	Selectivity in hydrocarbon (mol%)	Yield (mol%)					
			Nonane	Decenes	Decane	1-Decanol	1-Decanethiol	Other products
Mo/Al$_2$O$_3$	28.4	32	3.2	4.0	1.9	13.7	2.3	3.3
CoMo/Al$_2$O$_3$	46.2	58	3.8	17.5	5.5	11.5	5.9	2.0

on the catalyst, it was lower over CoMo/Al$_2$O$_3$ (equal to 0.3) than over Mo/Al$_2$O$_3$ (equal to 0.5), showing that cobalt favoured the formation of decenes probably by the increase of the dehydration rate of 1-decanol. In addition, the yield in nonane was similar over both catalysts since this hydrocarbon was only produced by thermal decomposition of decanal, as already discussed in this paper.

4. Conclusions

The present study showed that both CoMo and NiMo sulfided catalysts are efficient catalysts in deoxygenation of decanoic acid, C9 hydrocarbons (nonenes and nonane) obtained by dehydration and decarbonylation reactions (DEC pathway) being its main deoxygenated products. A second deoxygenation route, named hydrodeoxygenation (HDO), involved dehydration and hydrogenation reactions, and led to C10 hydrocarbons (decenes and decane) as ultimate deoxygenated products. The HDO way was the main route of the transformation of decanoic acid over the unpromoted (Mo/Al$_2$O$_3$) catalyst and was inhibited by Co and Ni.

The existence of a common intermediate between the two deoxygenation routes (HDO and DEC routes) was proposed. Such intermediate could be a cationic species adsorbed onto a sulfur vacancy which can be considered as an active site. The presence of Co or Ni in the sulfided phase is meant to increase the basicity of sulfur anions in the vicinity of Co or Ni, thus fostering the elimination step involved in the DEC pathway.

The study of the deoxygenation of decanoic acid used as a probe molecule should allow the modelling of deoxygenation of raw materials that can be vegetable oils. Enhancing its deoxygenation by the DEC route should ensure the reduction of the consumption of hydrogen during the upgrading of these bio-oils. This is the case when promoted sulfided solids were used as catalysts. Nevertheless, the strong adsorption of carboxylic acids on sulfided active sites, as highlighted in this work, would likely result in significant inhibiting effects of carboxylic acids on the deoxygenation of other oxygenated compounds.

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